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THE PREPARATION OF RING-SUBSTITUTED L-CHLOROACETOPHENONES

PART II

THE LARGE LABORATORY-SCALE PREPARATION OF
L-CHLORO-o-NITRO-ACETOPHENONE (o-NITRO-CN)

By

A.H. FORD-MOORE, L.J. LERMIT AND G.W. WOOD

PORTON TECHNICAL PAPER No. 354

C.D.E.E.
Porton
1954

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PORTON TECHNICAL PAPER NO: 354

DATE: 6 MAY 1953

THE PREPARATION OF RING-SUBSTITUTED α -CHLOROACETOPHENONES

PART II. The Large Laboratory-Scale Preparation of
 α -Chloro-o-nitroacetophenone (o-Nitro-CN)

by

A.H. Ford-Moore, L.J. Lemit and G.W. Wood

SUMMARY

Full experimental details are given for the preparation of α -Chloro-o-nitroacetophenone on a large laboratory-scale. The method described is based on o-nitrotoluene and avoids the dangerous distillation of the intermediate o-nitrobenzoyl chloride. It gives a final product of high purity in yields of about 55% based on the starting material.

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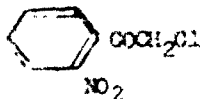
by

A.H. Ford-Moore, L.J. Lemit and G.W. Wood

Introduction

1. α -Chloro-o-nitroacetophenone (o-Nitro-CN; T.732; (I)), although less powerful than α -chloroacetophenone (CN) as a lachrymator, has aggressive and irritant properties so marked that it is a most valuable agent for testing the fit of respirator facepieces where a really accurate fit is essential.

The small scale preparation of the former substance was described recently in a Porcon Technical Paper (1). This method was based on the synthesis of o-nitroacetophenone as described in Organic Syntheses (2). The method consisted in reacting the magnesium salt of diethyl malonate with o-nitro-benzoyl chloride and hydrolysing the diethyl o-nitrobenzoyl-malonate so obtained.



(I)

This method was found to have many advantages over those already described (3). The yield was very good and the purity of the product excellent. The latter point was of particular importance since the m- and p-isomers on chlorination gave substances so inferior in aggressive properties as to be valueless as fitting agents.

Although one of the authors of the present report (A.H. Ford-Moore) found no difficulty in preparing o-nitrobenzoyl chloride from o-nitrobenzoic acid and also in distilling the product under reduced pressure, a firm that had undertaken the preparation of 1 Kg. of T.732 experienced two such disastrous explosions that they abandoned the project.

A visit to the firm in question failed to elicit the cause of these explosions with any certainty, but it seemed clear that the methods adopted, and also possibly the purity of the o-nitrobenzoic acid used, might have been contributory factors.

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Since Porton had had some considerable experience in the preparation of this substance, it was decided to prepare a quantity of it, using materials of unequivocal purity. As it seems possible that there may be a demand for this substance in the near future, comprehensive directions for its preparation are given in the Appendix.

2. The Preparation of o-Nitrobenzoic Acid

It seemed most probable that the risk of accident in the preparation of o-nitrobenzoyl chloride might be minimised, or even eliminated, by the use of a really high grade of o-nitrobenzoic acid. This is best obtained by the oxidation of pure o-nitrotoluene with potassium permanganate. The former substance can be purchased in a high state of purity and was distilled under reduced pressure through a helix-packed column before use. When o-nitrotoluene is added to a boiling solution of potassium permanganate, a very pure sample of the acid is obtained after one crystallisation from water. But this method has the drawback that the volume of the reaction product after filtering the manganese dioxide formed (ca. 4 litres) is very large compared with the yield of acid (ca. 110 g.). Since the latter has a very appreciable solubility in cold water, the volume has to be reduced to ca. 800 cc. before isolating the acid by acidification.

The exhaustive studies of Bigelow (4) on the oxidation of the three nitrotoluenes showed that in the case of the o-isomer, the maximum yield depended on various factors, the most important points being: (i) the reactants should be in the highest convenient dilution, since increasing concentration favoured not only the decomposition of unreacted permanganate but also the destructive oxidation of the acid formed; (ii) the presence of a small amount of free alkali at the start of the reaction has a marked accelerating effect on the speed of the oxidation; (iii) the optimum proportion of permanganate is about 10% excess of that demanded by theory. A greater excess tended to destroy the acid by further oxidation as fast as it was formed from the nitrotoluene. For the same reason, it is particularly important to add the oxidising agent to the nitrotoluene so as to avoid further oxidation of the acid by the permanganate when the reverse order of addition was followed.

(i) and (ii) have received ample confirmation in this laboratory. In an attempt to reduce the bulk of the reaction mixture, the amount of water taken was halved. As a result, a marked falling off in the yield of acid was noticed. Moreover, when the oxidation was carried out in the presence of magnesium sulphate (so as to maintain neutrality during the oxidation), poorer yields were again obtained.

Accordingly, an alternative method, based on that of Reimer and Gatewood (5), was worked out. Certain modifications were introduced so that it could be scaled up sevenfold and also run on a semi-continuous basis. The slightly lower yields (76% as against 85 - 90% claimed by Reimer and Gatewood) were more than compensated by the saving of time, labour and laboratory services.

Broadly speaking, it consisted of adding solid permanganate to a stirred, boiling suspension of nitrotoluene in very dilute sodium hydroxide

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solution. At the end of the reaction, the manganese dioxide and unreacted nitrotoluene settled to the bottom of the reaction vessel in the form of a compact sludge and the clear alkaline solution of the nitrobenzoic acid was decanted. The sludge was filtered, the unreacted nitrotoluene separated for use in a subsequent run and the aqueous portion added to that already decanted. The manganese dioxide was then washed, the washings being used to provide the necessary alkali and part of the water in a subsequent run.

The main aqueous portion was then fed into an evaporator for concentration and finally acidified with concentrated hydrochloric acid. After standing in an ice box overnight, the nitrobenzoic acid was filtered and recrystallized from boiling water. Although the finished product was not quite so pure as that obtained in Method (1) (Appendix), it was quite pure enough for conversion to the acid chloride. Furthermore, the tedious recovery of the unreacted nitrotoluene is avoided.

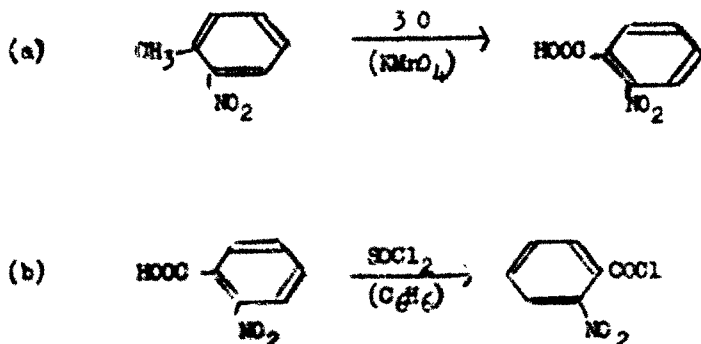
3. The Preparation of o-Nitrobenzoyl Chloride

Using o-nitrobenzoic acid prepared as described in the previous paragraph, no trouble was experienced in preparing the chloride, though it was considered advisable to distill the thionyl chloride used through a helix-packed column. For a preparation on a three-molar scale, the reaction was carried out in dry benzene, diluent and excess of thionyl chloride being removed under diminished pressure at the end of the reaction. It was found unnecessary to distill the nitrobenzoyl chloride since it solidified completely at the end of the operation.

4. The Preparation of o-Nitroacetophenone and T.732

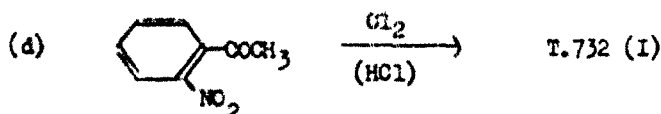
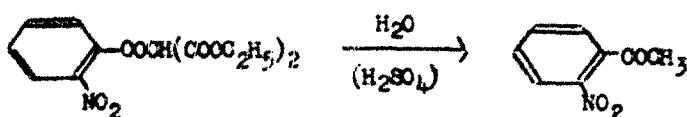
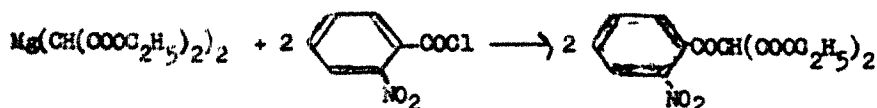
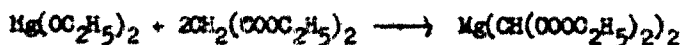
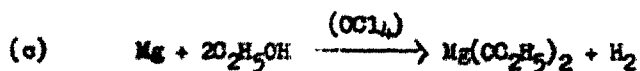
These two stages of the synthesis call for no comment. It is sufficient to say that, in the preparation of the former, a three-molar run can be carried out without difficulty. Even when the undistilled chloride was used, the nitroacetophenone crystallized completely in the receiver on vacuum distillation. Its melting point showed that it was in a very high state of purity. The final chlorination to T.732 was carried out as described in the relevant Porter Technical Paper (1).

The train of operations from o-nitrotoluene to T.732 (I) is as follows:



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Summary

5. The preparation of T.732 on a large laboratory scale presents no difficulty. The following points may be noted: (1) o-nitrobenzoic acid of a high degree of purity is essential. When this is assured, no further trouble is experienced. Material of this purity may be obtained by the permanganate oxidation of o-nitrotoluene, followed by one crystallisation from water.

When acid of high purity is used, the acid chloride, obtained by the action of redistilled thionyl chloride in benzene, does not require distillation.

Using the magnesium-malonic ester synthesis, the o-nitroacetophenone is obtained in a high state of purity, even though the acid chloride is used without distillation.

If the experimental conditions described in this report are adhered to, there is no risk of explosions during the preparation.

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6. The authors wish to acknowledge the most useful suggestions and practical assistance of C. Stratford and R.V. Ley.

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APPENDIX

Experimental

1. o-Nitrobenzoic Acid

Method (1)

Potassium permanganate (512 g.) and water (4 L.) are placed in a 6-litre 3-necked Pyrex flask fitted with a powerful stainless steel stirrer, an efficient condenser (Note 1) and a dropping funnel carrying o-nitrotoluene (redistilled, b.p. 63 - 64°/3 mm.; n_D^{20} 1.5440; 176 g. = 160 cc.). The stirrer is started and the mixture heated to boiling over a ring burner and wire gauze. When boiling, about 20 cc. of the nitrotoluene are introduced. As soon as the vigorous oxidation sets in, the burner is extinguished and the rest of the nitrotoluene run in at such a rate that rapid boiling is maintained. When the addition is complete, the burner is relit and the mixture refluxed, with continued stirring, till the permanganate is used up (Note 2). This requires about 1 hour.

The condenser is then set for distillation, the dropping funnel replaced by a steam inlet and unreacted nitrotoluene removed by steam distillation (Note 3). About 50 - 60 cc. are recovered. After cooling, the mixture is filtered, using a large sintered-glass funnel and a 10 litre filter flask. The manganese dioxide on the filter is well pressed down and washed with 1 litre of hot water.

The filtrate is then concentrated to ca. 800 cc. by distillation from a steam bath with the aid of a water pump, a 2-litre distilling flask is used and the filtrate transferred gradually from the filter flask by means of a siphon tube and stopcock. The residue, after filtering if necessary, is added to a mixture of hydrochloric acid (d 1.18; 400 cc.) and about 600 g. of ice cubes. The precipitated acid is filtered and washed with about 250 cc. of cold water. The wet product (Note 4) is recrystallized from boiling water (ca. 700 cc.). After cooling in the ice-box overnight, the pure acid is filtered and dried in a steam oven. The yield is 85 - 96 g. (69 - 74%, based on the nitrotoluene used up (Note 5)), m.p. 143 - 149°.

NOTES

1. To avoid choking during the vigorous reaction, the condenser should be of wide bore, preferably of the double internal coil type.
2. This may be determined by withdrawing a drop of reaction mixture with a glass rod and spotting a piece of filter paper. Absence of any trace of pink on the perimeter of the black spot indicates that the reaction is complete.
3. In order to facilitate the removal of the nitrotoluene by steam distillation, the reaction flask should be heated. It is essential that stirring is maintained throughout as, without this, the violent bumping caused by the manganese dioxide may easily lead to the fracture of the flask.

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4. The precipitated acid retains a considerable quantity of water mechanically. It is quickest to recrystallize without drying. The mother liquor from the crystallization should be used from crystallizing subsequent batches since *o*-nitrobenzoic acid is appreciably soluble in cold water.

5. Recovered *o*-nitrotoluene may be used in subsequent runs.

Method (ii)

o-Nitrotoluene (274 g.; 236 cc.; 2 moles), sodium hydroxide (20 g.; 0.5 mole) and water (2.5 litres) are mixed in a 5-litre 3-necked flask fitted with an efficient stirrer and a long wide-bore reflux condenser (approximately 30" x 1" inside diameter). The suspension is stirred and heated to boiling. The source of heat (Note 1) is then reduced and solid potassium permanganate (695 g.; 2.2 moles) introduced in portions down the condenser, with the occasional assistance of a glass rod in the event of clogging, as rapidly as is consistent with the effective reflux control of the reaction. A small, constant supply of heat is maintained throughout to ensure that the temperature of the mixture does not fall below boiling point (Note 2). When the last of the permanganate has completely reacted, stirring and heating are discontinued and the mixture allowed to cool. The manganese dioxide and unreacted nitrotoluene settle out cleanly and rapidly as a distinct lower layer from which the bulk of the clear alkaline *o*-nitrobenzoic acid is decanted. This is fed into an evaporator and concentrated on a steam bath under reduced pressure till the accumulated salts begin to crystallize.

The sludge of manganese dioxide and nitrotoluene is filtered and the filter cake washed with hot water, the washings being kept separate from the main filtrate. Unreacted nitrotoluene is removed from the filtrate and from the washings (Note 3), the filtrate being added to the main bulk of the alkaline nitrobenzoate solutions and the washings being used to supply the necessary alkali and part of the water in a subsequent run.

The concentrated alkaline nitrobenzoate solution is then acidified to Congo Red with hydrochloric acid (d 1.18) (Note 4) and, after standing overnight in an ice box, the nitrobenzoic acid filtered and washed once with cold water. It was crystallized from boiling water and, after drying at 100°, melted at 142°. It was sufficiently pure for conversion to the acid chloride. All filtrates are combined and worked up by concentration under reduced pressure. The average yield from each of six such runs is 195 g. (76% based on the nitrotoluene actually consumed)

NOTES

1. A ring burner and an asbestos-gauze mat was used; provided that continuous and efficient stirring is maintained throughout the period of heating, there is no risk of trouble being caused by the caking of the manganese dioxide on the bottom of the flask.

2. Once started, any serious delay or interruption in the addition of the permanganate, resulting in cooling and subsequent re-heating to reflux temperature, causes a marked decrease in the yield of product.

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3. The unchanged nitrotoluene thus recovered is in a state of purity sufficiently high for use without further purification in subsequent runs. The average recovery for six runs is 64 g. (55 cc.) per run.

4. Hydrochloric acid is better than 50% sulphuric acid. In later runs, the accumulation of the relatively sparingly soluble potassium sulphate was such that it tended to crystallise out in preference to the nitrobenzoic acid. The greater solubility of potassium chloride obviates this difficulty.

2. o-Nitrobenzoyl chloride

Redistilled thionyl chloride (300 cc.) is added with gentle swirling to a mixture of dry o-nitrobenzoic acid (471 g.) in dry benzene (1350 cc.) (Note 1) contained in a 3 litre round flask. The flask was then fitted with a reflux condenser protected with a calcium chloride guard tube and the mixture heated to gentle refluxing in an oil bath for 2 hours. Copious quantities of sulphur dioxide and hydrogen chloride are at first evolved but after about 90 minutes these have practically ceased. The condenser was then set for distillation and the benzene and excess thionyl chloride recovered under somewhat reduced pressure, care being taken to keep the temperature of the oil bath below 85° (Note 2). The last traces of thionyl chloride are removed in vacuo, small quantities of dry benzene (4 x 50 cc.) being used as an entrainer. The oily residue after heating on an oil bath (temperature below 85) at 0.1 mm. for 2 hours is allowed to stand in a stoppered flask in a cool place overnight. It then set to a mass of small crystals, m.p. 23°. Yield 504 g. (98.5% on the o-nitrobenzoic acid).

NOTES

1. The use of benzene as a diluent serves to moderate the violence of the reaction and ensures that the reaction temperature does not rise above 85°.

2. o-Nitrobenzoyl chloride should not be heated above 100° as, above this temperature it has been known to decompose explosively. (6), (7).

3. o-Nitroacetophenone

The reaction is carried out in a 10-litre 3-necked flask equipped with two reflux condensers of large capacity, an efficient stirrer and a dropping funnel. The whole apparatus should be dried in a warm oven overnight and was protected from atmospheric moisture with calcium chloride guard tubes.

Clean, dry magnesium (75 g.), anhydrous ethanol (72 cc.) carbon tetrachloride (dried over phosphorus pentoxide) (4.5 cc.) and a trace of iodine dissolved in sodium-dried ether are placed in the flask. It is warmed cautiously till a vigorous exothermic reaction sets in, during which sodium dried ether (2205 cc.) is added and the flask heated on a warm water bath so that the ether refluxes quietly. To the rapidly stirred

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solution is added a mixture of redistilled ethyl malonate (443 g.; 420.3 cc.), anhydrous ethanol (292.5 cc.) and dry ether (360 cc.), the addition taking about 0.5 hour. The heating was continued for 3 hours, by which time all the magnesium has dissolved and a light grey solution obtained. Stirring is maintained throughout the operation.

o-Nitrobenzoyl chloride (504 g.) in dry ether (600 cc.) is then added over a period of 15 minutes to the rapidly stirred solution. Towards the end of the addition, the reaction mixture becomes green and a sticky solid separates out. Stirring becomes very difficult and at the end of the addition had ceased. After cooling to room temperature, a cold solution of concentrated sulphuric acid (202.5 cc.) in water (292.5 cc.) is added slowly. The reaction mixture is stirred for 0.5 hour by which time it had formed two layers. The ether layer is separated and the water layer extracted with ether (3 x 400 cc.). The ether from the combined ether layers is recovered by distillation from a steam bath, the syrupy residue treated with a mixture of glacial acetic acid (900 cc.), concentrated sulphuric acid (111.6 cc.) and water (565 cc.) and the whole heated under gentle reflux for 4.5 hours. The reaction mixture is cooled, finally in ice, and made alkaline with 20% aqueous sodium hydroxide (Note). The resulting mixture is extracted with ether until it no longer smells of the product, the ether extracts combined, dried with anhydrous magnesium sulphate and the ether removed on a steam bath. The dark residue is purified by distillation under reduced pressure from a Koni flask fitted with a 14" Lapworth column. The yield of pure *o*-nitroacetophenone, b.p. 104 - 106°/4 mm. is 377 g. (76.5% based on the *o*-nitrobenzoic acid or 58% based on the *o*-nitrotoluene). It has the following physical constants; f.p. 25°; n_D^{25} 1.5476.

NOTE

The use of a large excess of sodium hydroxide should be avoided as this appears to bring about some decomposition.

4. 3-Chloro-*o*-nitroacetophenone

A solution of chlorine is prepared by passing the gas through a sintered glass distributor into a mixture of glacial acetic acid (450 cc.) and hydrochloric acid (d. 1.18; 50 cc.) until saturated. This takes about 2 hours. The strength of this solution is determined by adding an aliquot portion to an excess of potassium iodide and estimating the liberated iodine with sodium thiosulphate.

o-Nitroacetophenone (51 g.) in glacial acetic acid (50 cc.) is added to an appropriate amount of chlorine-acetic acid-hydrochloric acid mixture (= 1.1 mole of the latter) and the mixture allowed to stand in a fume cupboard at room temperature. The temperature of the mixture gradually rises and finally reaches 41° after 2 hours, by which time the yellow colour of the chlorine solution has disappeared. The mixture is then concentrated in vacuo on a steam bath to give a clear syrup. This is digested with warm petrol (b.p. 40 - 60°), cooled to 0° and filtered. The yield of product is 62 g., m.p. 57 - 61° (Note).

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NOTE

A purer product may be obtained (m.p. 64 - 65°) by crystallising from methanol, followed by strong cooling. This is attended by some loss and the unpurified product is good enough for most purposes.

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